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(54) Title: METHODS FOR REDUCING THE FLAMMABILITY OF CELLULOSIC SUBSTRATES (57) Abstract <p>Methods of rendering cellulosic materials fire retardant, and articles of manufacture including the materials, are disclosed. The methods involve applying a flame retardant composition to the material. In one embodiment, the composition includes a carboxylic acid-containing compound in the substantial absence of a phosphorous-based esterification catalyst or a basic, (i.e., metal alkoxide) catalyst. The material is heated to esterify at least a portion of the hydroxy groups. In another embodiment, the compositions include an amino acid, protein and/or peptide and optionally include one or more crosslinking and/or coupling agents. Enzymes are a preferred protein. The methods involve applying the composition to the material, and optionally involve covalently linking the amino acid, protein and/or peptide to the material, either directly or via a crosslinking agent. In a third embodiment, the compositions include one or more crosslinking agents, and optionally, one or more phosphorus-based compounds. Dimethyloldihydroxyethylene urea, imidazole, imidazolidinones, dialdehydes, and dichlorotriazines are preferred crosslinking agents. The methods involve applying the composition to the material, and covalently linking the crosslinking agent to the material. An advantage of covalently linking the crosslinking agent to the cellulosic material is the lack of any potential toxicity associated with uncrosslinked fire retardants on the cellulosic material and the stability of the bonds between the material and the crosslinking agent to conventional steam cleaning and other carpet cleaning methods. In a preferred embodiment, the fire-retardant cotton-fiber composition is used to prepare cotton carpets or raised surface and lightweight apparel.</p>		

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METHODS FOR REDUCING THE FLAMMABILITY OF CELLULOSIC SUBSTRATES

FIELD OF THE INVENTION

5 The present application relates to methods for reducing the flammability of cellulosic substrates, including cotton fiber carpets and raised surface and lightweight apparel.

BACKGROUND OF THE INVENTION

10 Cotton, like most textile fibers, is combustible. Whenever cotton is in the presence of oxygen and the temperature is high enough to initiate combustion (360-420°C), untreated cotton will either burn (flaming combustion) or smolder (smolder combustion). The degree of flammability depends on the fabric construction. Fabrics have different flammability
15 requirements depending on the particular end use. Cotton fabrics, without the use of special flame-retardant finishes, meet practically all of these requirements for most existing end-uses. However, some new cotton product developments require special constructions or finishes to reduce their flammability. This is especially true in certain countries, such as the United
20 States, which have strict regulations governing the flammability of these products.

Resistance to burning is one of the most useful properties that can be imparted to cotton fibers and textiles. Some end uses for cotton in textiles for
25 apparel, home furnishings, and industry, can depend on its ability to be treated with chemical agents (flame-retardants) that confer flame resistance (FR). End uses requiring flame-retardant finishes include protective clothing (e.g., foundry workers apparel and fire fighters uniforms), children's sleepwear, furnishing/upholstery, bedding, carpets, curtains/drapes, and
30 tents.

Chemical agents for reducing the flammability of products containing cotton fiber and other cellulosic fibers are well known and generally grouped into two categories: durable and non-durable. The durable type tend not to be removed in conventional washes and the non-durable type are typically removed in conventional washes.

The variable manufacturing cost of a typical durable flame-retardant treatment is about \$1-2 per yard, depending on fabric weight and other factors. This can be a major limitation. The flammability and flame resistance of cotton has been studied extensively and several comprehensive reviews of the subject are available.

Cotton is not currently the raw material of choice in the carpet industry. The carpet fiber business in the U.S. is roughly a 5,000,000 bale/year market, and cotton is less than one percent of this overall market. One reason that cotton has been almost excluded from this large market for fibers is the difficulty in complying with the Flammable Fabrics Act. This regulation requires that all carpets which are six feet by four feet or larger and are sold for residential use pass a flammability test. This test is commonly referred to as the "Pill Test". It calls for igniting a methenamine pill, which is placed in the center of a nine-inch by nine-inch carpet specimen. The specimen fails if the flame spreads to within one inch of a metal template containing an eight-inch diameter hole, which is placed on top of the carpet specimen prior to igniting the pill. The specimen passes if the flame does not spread to within one inch of the metal template.

For a residential carpet to be saleable, at least seven out of eight specimens must pass the test. Furthermore, if the carpet has been treated with a flame-retardant (with the exception of alumina trihydrate added to the back coating), then the carpet must be washed ten times as described in AATCC 124-1967 prior to testing.

There are numerous man-made fiber carpets which are currently available, many of which do not require any special treatments to pass federal flammability requirements because of the nature of the test. Many synthetic carpet fibers will melt away from the burning pill during the pill test, such that the pill eventually self extinguishes. The fuel load provided by these carpets in a fire, which is already burning, is not considered by the test method.

Other synthetic fiber carpets, such as polypropylene, require a flame-retardant such as alumina trihydrate. Alumina trihydrate is often added to a backcoating (or backing), as opposed to application directly to the carpet fibers. Synthetic thermoplastic fibers such as polypropylene melt quickly when exposed to a flame, for example, during the pill test. The burning pill then quickly falls, due to gravity, onto the backing. The backing typically includes three layers: a thermoplastic (usually polypropylene) primary backing layer, a latex adhesive layer (which may contain the flame-retardant) and a secondary thermoplastic (usually polypropylene) backing layer. Since the primary backing is also a low melting point thermoplastic, it quickly melts and allows the burning pill to come into direct contact with the latex. Since the latex often includes a flame-retardant, it can then suppress the spread of flames.

Certain other fibers, such as wool and modacrylic, are inherently flame resistant. These can be made into carpets which require no special treatments to pass the required pill test.

Cotton carpets can also be made which require no special treatments to pass the pill test. For example, a cut pile carpet can be made from a 3/2 Ne yarn composed of 90 percent cotton and 10 percent low melt thermoplastic fiber. The low melt fiber is allowed to melt, typically prior to tufting of the carpet. A carpet which includes 12 stitches per inch, 1/11-inch

gauge, and ¼ inch pile height can be constructed from this yarn. Such a carpet is generally dense enough, with a sufficiently low pile height, that it will pass the pill test without any additional treatment.

5 A disadvantage of relying on such low pile height constructions when manufacturing cotton carpets is that it is very limiting from a design and marketing standpoint. The consumer in the U.S. today has become accustomed to a wide variety of choices when selecting a carpet. Substantially limiting the choices of carpet construction is not a practical
10 option for a successful marketing program.

 Another disadvantage of attempting to reduce the flammability of a cotton (or cellulosic) carpet by construction alone is that achieving reduced flammability often means increasing the area density (oz./ square yard) of the
15 carpet. As the area density of the carpet increases, the cost also generally increases. This approach is therefore very restrictive and would limit the market to the small, upper price end.

 Alumina trihydrate, which is effective on certain thermoplastic fiber
20 carpets, is not typically effective on cotton-containing carpets. On cotton-containing carpets, the cotton yarn which is under and in the vicinity of the burning pill will tend to char but maintain sufficient integrity to support, insulate and separate the burning pill from the carpet backing. There is not a sufficient heat flux reaching the alumina trihydrate contained in the latex
25 backing for the alumina trihydrate to be effective at suppressing the flame.

 The use of flame-retardant low melt fibers in place of the typical non-flame-retardant low melt fiber used in the yarn has been attempted. The low melt fiber, in general, offers the advantages of improved resilience and tuft
30 definition and minimizes shedding of loose fibers from the tufts. Testing has shown that flame retardant low melt fiber used in the yarn is not effective.

Although various explanations have been offered, the mechanism is not understood.

5 Since federal law in the U.S. requires that any carpet which has a flame-retardant treatment (other than alumina trihydrate) be laundered ten times prior to flammability testing, any such flame-retardant which is applied for that purpose must remain effective after the ten home launderings. Because home launderings are rather effective at removing materials which are not chemically bonded to the fibers, durable flame retardants are
10 generally the most effective.

There have been many techniques for imparting durable flame resistance properties to cellulosic substrates described in the literature. However, there are relatively few that are practiced today, due to commercial
15 availability of the chemicals, safety concerns, process control issues or other reasons. Durable flame retardants are typically more complex, more expensive and more difficult to apply than non-durable treatments. The main flame retardant finishes used on cotton are phosphorus-based.

20 Two of the more common phosphorous-based systems which are used to provide durable flame resistance to cotton substrates are the "pre-condensate"/ammonia process and the reactive phosphorous process.

In the "pre-condensate" /NH₃ process, the flame-retardant agent
25 exists as a polymer in the fibrils of cotton fibers and is not combined chemically with OH groups in the cotton fiber. This process imparts durable flame resistance to 100% cotton fabrics when applied under proper application procedures. It produces fabrics with a good hand and strength retention. Proper application of pre-condensates to cotton fabrics requires
30 adequate fabric preparation, proper padding/uniform application, proper phosphorus add-on relative to fabric properties, appropriate moisture control

prior to ammoniation, control of the ammoniation step to ensure adequate polymer formation, and effective oxidation and washing of the treated fabric.

This process is very useful for specialty applications that can
5 command a very high price, such as protective clothing for fire fighters and other workers who may be exposed to fire or excessive heat. It is generally not practical for cotton carpets or raised surface or lightweight apparel that will be sold to the average consumer. The problems associated with this process include the high cost, the special equipment needed (ammoniation
10 chamber) which is not generally available, and the two drying steps which are required.

Reactive phosphorus-based flame retardants are compounds (e.g., N-methylol dimethyl phosphonopropionamide (MDPPA)) that react with
15 cellulose, the main constituent of cotton fiber. These compounds can be used both for cotton and for cotton blends with a low synthetic fiber content. The finish, usually applied to the fabric after the coloring stage, promotes char formation. The durability of the finish makes the resulting treated fabric suitable for curtains, upholstery, bed linen and protective clothing.

20

The reactive phosphorus-based flame retardants are typically applied using a pad/dry/cure method, in the presence of phosphoric acid catalyst. The finish is sometimes applied with a methylated melamine resin to increase the bonding/fixation of the agent to cellulose, which enhances the
25 flame retardancy. Afterwashing is generally required, often with an alkali such as soda ash, followed by further rinsing and drying. The afterwashing helps to reduce loss of fabric strength. The reactive phosphorous-based process has the advantage of not requiring specialized equipment such as an ammonia cure unit, and has less affect on dyes than the pre-condensate
30 process. However, this process can cause more strength loss than the pre-condensate process. Further, there can be a durability problem associated

with some wash treatments if the instructions of the chemical supplier are not followed.

Reactive phosphorus based flame retardants can be unsuitable for certain end uses, such as cotton or cotton blend carpets. This is especially true when the products contain formaldehyde, because of concerns about the human health effects of exposure to certain volatile organic compounds (VOC's) which may have been released from carpeting or carpet backing in past years. Because of this, most carpet manufacturers generally consider even very low levels of formaldehyde to be unacceptable. Another issue is that these products are generally designed to be afterwashed as part of the application procedure. While the toxicity of such materials is generally low, there are significant concerns about the exposure of babies or small children to residual unfixed chemicals left on the carpet.

15

One non-phosphorous approach for rendering cotton fire retardant has been to incorporate a water-insoluble, solid particulate mixture of brominated organic compounds and metal oxides, optionally with a metal hydrate, into the carpet fiber (U.S. Patent No. 4,600,606 to Mischutin). However, a limitation of the chemistry is that the metal oxide compounds may be rendered soluble when washed if the pH of the solution is on the acid side. Also, particles of brominated organic compounds may be irritating to people coming into contact with them, and may be harmful if ingested.

20

Another non-phosphorous approach has been to prepare a solution of boric acid, ammonium sulfate, borax, hydrogen peroxide, and optionally a surfactant and/or an alkyl phthalate ester, and apply this as a coating on cellulosic materials. A major limitation of this chemistry is the water-solubility of the components, which results in the composition being substantially removed during conventional washing.

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U.S. Patent Nos. 4,820,307, 4,936,865 and 4,975,209 to Welch et al., and U.S. Patent No. 5,221,285 to Andrews et al., the contents of which are hereby incorporated by reference in their entirety, disclose using carboxylic acid-containing compositions to crosslink fibrous cellulosic textiles and provide the textiles with wrinkle resistance, smooth drying properties and durability to repeated laundering in alkaline detergents (see, for example, the Abstracts of each of the patents). The methods disclosed in these patents require using phosphorous-based catalysts, and tend to provide a high degree of esterification on the cellulosic textiles, which is advantageous for imparting wrinkle resistance but which may provide too high a degree of esterification for other uses.

Because wrinkle resistance is not usually a sought after property for carpets, carpets have not been treated with the carboxylic acid treatments described in the Welch and Andrews patents. Further, with respect to cotton-based raised surface and lightweight apparel, the relatively high concentration necessary to impart wrinkle resistance would also be expected to adversely affect the "hand" of the resulting fabrics. When used in a concentration which would provide acceptable hand to cotton-based raised surface and lightweight apparel, the wrinkle resistance may not be acceptable.

There is a need for fire retardants for cotton fiber, especially when the fiber is used in a cotton carpet or in raised surface and lightweight apparel, that survives a certain number of washings, including steam cleanings. The present invention provides such materials.

SUMMARY OF THE INVENTION

Methods for providing cellulosic fibers or products made of cellulosic fibers, with reduced flammability, are disclosed. Cotton is a preferred cellulosic fiber. Other cellulosic fibers include flax, jute, hemp,

ramie, Lyocell, Tencell™ and regenerated unsubstituted wood celluloses such as rayon.

5 In Embodiment A, the methods involve applying to a cellulosic fiber or products made from cellulosic fibers, a composition which includes a carboxylic acid but which does not include a significant amount of a phosphorous-based esterification catalyst or a basic catalyst (i.e., a metal alkoxide) and reacting some or all of the carboxyl groups with some or all of the hydroxy groups present on the cellulosic fiber. The carboxylic acid is
10 one which is capable of reacting with a cellulosic substrate when heated to a temperature of between 100 and 200°C for between 15 and 30 minutes or less in the substantial absence of a phosphorous-based catalyst or a basic catalyst.

15 Preferably, the carboxylic acid is maleic, malic, tartaric, succinic or citric acid, and can be in the form of carboxylic acid-containing polymers such as maleic acid/acrylic acid copolymers.

The carboxylic acids and hydroxy groups are linked via ester linkages
20 by heating the acid-treated cellulosic fibers, preferably to a temperature of between 100 and 200°C for between 15 minutes and 30 minutes or less. The esterification is performed in the substantial absence of phosphorous-based or basic (for example, metal alkoxide) catalysts. The absence of phosphorous-based catalysts avoids the presence of phosphorous-based
25 materials in the final product, and also facilitates imparting a relatively low degree of esterification on the cellulosic material. The absence of basic catalysts increases the rate of reaction, which can be preferred when longer reaction times cause adverse reactions or are not practical.

30 When the composition is applied to the cellulosic substrate, the percent by weight of the fire retardant solution which is applied to the

cellulosic substrate is typically between about 1.0 and 200 percent by weight, preferably between about 5.0 and 100 percent by weight, and more preferably, between about 15 and 80 percent by weight of the fiber to be treated. These ranges vary depending on the mode of application and the
5 cellulosic substrate to be treated. For example, for raised surface and lightweight apparel, larger amounts of the fire retardant solution may be required to achieve adequate fire resistance. This same general principal, of adjusting the solution concentration based on the total wet add-on, applies to other substrates as well, such as fiber fill or upholstery.

10

The resulting cellulosic fiber is fire resistant and the ester linkages between the carboxyl groups and the hydroxy groups on the cellulosic fiber are stable to most conventional washings, including the ten home
laundryings specified in 16 C.F.R. 1630 and 1631 for carpets which have
15 been treated with a flame retardant.

In embodiment B, the methods involve applying to a cellulosic fiber or products including a cellulosic fiber a composition which includes one or more amino acids, proteins and/or peptides, and optionally include one or
20 more crosslinking and/or coupling agents. The methods involve applying to a cellulosic fiber a composition including an amino acid, protein and/or peptide, and optionally involve chemically combining the amino acid, protein and/or peptide to the hydroxy groups on the cellulosic fiber using crosslinking and/or coupling agents.

25

Suitable amino acids include naturally-occurring and synthetic amino acids. The amine group can be at a position alpha to the carboxylic acid group, or can be at positions other than or in addition to the alpha position. Many amino acids include reactive groups such as hydroxy groups, thiols,
30 amines, and carboxylic acids. Carboxylic acids are known to react with hydroxy groups under various coupling conditions using known coupling

agents to form ester linkages. Thiols, amines and hydroxy groups on amino acids, proteins and/or peptides do not react directly with the hydroxy groups on the cellulosic materials, but can be covalently linked via crosslinking agents. Preferred amino acids are those which are commercially available in large quantities, for example, lysine and arginine.

Proteins and peptides are prepared by forming peptide (amide) bonds between various amino acids. Suitable proteins include soy proteins, milk proteins such as casein, derivatives thereof, and enzymes. In a preferred embodiment, the protein is an enzyme. Suitable enzymes include cellulases, lipases, catalases, amylases, proteases, pectinases, xylanases, isomerases and beta-glucanases.

The crosslinking agents are reactive molecules which include two or more leaving groups, such that a thiol, amine and/or hydroxy group on the amino acid, protein and/or peptide can react with one of the groups, and the other group can react with a hydroxy group on a cellulosic material. Examples of suitable crosslinking agents include dichlorotriazines, ureas, imidazolidinones, imidazoles, dialdehydes, divinyl sulfones, urethanes, carbonates, orthocarbonates, chloroformate, dihalides such as 1,2-dichloroethane, diesters such as dimethylsuccinate, diacid halides such as succinyl chloride, and the like.

The carboxylic acids on the amino acids, proteins and/or peptides and the hydroxy groups on the cellulosic substrate can be linked via ester linkages with or without the use of coupling agents. In one embodiment, the esterification is performed using a catalyst and heat, using the esterification conditions disclosed in U.S. Patent No. 4,820,307 to Welch et al., the contents of which are hereby incorporated by reference.

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Conventional esterification conditions, for example, forming acid

halides and reacting the acid halides with the hydroxy groups on the cellulosic material in the presence of a tertiary amine, can also be used. This embodiment can be less preferred, due to the higher cost of the raw materials.

5

When the composition is applied to the cellulosic substrate by spray or foam, the percent by weight of the fire retardant solution which is applied to the cellulosic substrate is typically between about 5 and 100 percent by weight, preferably between about 10 and 50 percent by weight, and more preferably, between about 15 and 30 percent by weight of the fiber to be treated. These ranges vary depending on the mode of application and the cellulosic substrate to be treated. For example, for raised surface and lightweight apparel, larger amounts of the fire retardant solution may be required to achieve adequate fire resistance. This same general principal, of adjusting the solution concentration based on the total wet add-on, applies to other substrates as well, such as fiber fill or upholstery.

The amino acids, proteins and/or peptides can also be applied by other application techniques including exhaust. In an exhaust application the liquor ratio may vary over a broad range of about 2 to 1 up to about 50 to 1. More preferably about 3 to 1 to about 20 to 1, meaning about 20 pounds of treating solution per pound of cellulosic containing substrate. In one preferred embodiment the liquor ratio is about 10 to 1 and the amino acid, protein and/or peptide concentration is adjusted accordingly down to a concentration ranging from 0.001 percent to about 5.0 percent and preferably from about 0.01 to 1.0 percent on the weight of the treating liquor which is equivalent to 0.1 percent to 10.0 percent on the weight of the cellulosic substrate. Wet coupling or crosslinking agents, which can also be applied by exhaust techniques from the same bath, can be applied with proteins, enzymes or amino acids to provide covalent linkages which result in treatments which are durable to various cleaning techniques. One such wet

crosslinking agent is known as T-DAS, a dichlorotriazine.

In embodiment C, the methods involve applying to a cellulosic fiber or substrate a composition which includes one or more crosslinking agents and optionally include one or more phosphorus-based compounds, such as phosphorus oligomers. The methods involve applying to a cellulosic substrate a composition including a crosslinking agent, optionally in the presence of a phosphorus-based compound, and covalently linking the hydroxy groups on the cellulosic substrate to one or more of the groups on the crosslinking agent.

The crosslinking agents are reactive molecules which include two or more reactive groups, which are capable of reacting with the hydroxy groups on cotton, or with derivatives formed from the hydroxy groups on cotton, for example, mesylate, triflate, and tosylate leaving groups. Suitable groups on the crosslinking agent for reacting with hydroxy groups on a cellulosic substrate include typical leaving groups in nucleophilic displacement chemistry and similar displacement chemistries. Suitable groups on the crosslinking agent for reacting with derivatives of the hydroxy groups on a cellulosic substrate such as mesylates and triflates include typical nucleophiles in nucleophilic displacement chemistry and similar displacement chemistries. Examples of suitable crosslinking agents include dichlorotriazines, ureas, imidazolidinones, imidazoles, dialdehydes, urethanes, carbonates, orthocarbonates, chloroformate, dihalides such as 1,2-dichloroethane, diesters such as dimethylsuccinate, diacid halides such as succinyl chloride, and the like.

The phosphoric acids and other reactive phosphorus-containing functional groups on the phosphorus-based compounds and the hydroxy groups on the cellulosic substrate can be linked via the crosslinking agents.

In all of the above embodiments, the treated fiber can be present alone or as blends of cotton and other commercially available fibers, including polyester (an example of which is polylactic acid polymers). The fibers can be used to prepare suitable articles of manufacture, including
5 carpets, raised surface and lightweight apparel, other garments, upholstery, and other articles which have acceptable fire resistance based on required tests for that particular use. In a preferred embodiment, the fiber is cotton and the article of manufacture is a cotton-based carpet or raised surface and lightweight apparel. The treated cotton carpets can have a density between
10 about 20 oz/yd² and 120 oz/yd², preferably between about 30 oz/yd² and 80 oz/yd².

In all of the above embodiments, the compositions can optionally include additional components, such as other fire retardants, dyes, wrinkle
15 resist agents, de-foaming agents, buffers, pH stabilizers, fixing agents, stain repellents such as fluorocarbons, stain blocking agents, soil repellents, wetting agents, softeners, water repellents, stain release agents, optical brighteners, emulsifiers, and surfactants.

20 DETAILED DESCRIPTION OF THE INVENTION

Methods for providing cellulosic fibers or substrates, in particular, cotton fibers, with reduced flammability, and articles of manufacture prepared from the resulting flame resistant cellulosic fibers, are disclosed.

25 In embodiment A, the methods involve applying to a cellulosic fiber a composition including a carboxylic acid, preferably selected from the group consisting of maleic acid, malic acid, tartaric acid, succinic acid, citric acid, and maleic acid/acrylic acid copolymers, and a suitable solvent, but not including a significant amount of a phosphorous-based esterification catalyst
30 or a basic catalyst (i.e., a metal alkoxide) and reacting some or all of the carboxyl groups with some or all of the hydroxy groups present on the

cellulosic fiber.

5 In embodiment B, the methods involve applying to a cellulosic fiber a composition which includes one or more amino acids, proteins and/or peptides, and optionally include one or more crosslinking and/or coupling agents. The methods involve applying to a cellulosic fiber a composition including an amino acid, protein and/or peptide, and optionally involve chemically combining the amino acid, protein and/or peptide to the hydroxy groups on the cellulosic fiber using crosslinking and/or coupling agents.

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In embodiment C, the methods involve applying to a cellulosic fiber a composition which includes one or more crosslinking agents and optionally include one or more phosphorus-based compounds, such as phosphorus oligomers. The methods involve applying to a cellulosic substrate a composition including a crosslinking agent, optionally in the presence of a phosphorus-based compound, and covalently linking the hydroxy groups on the cellulosic substrate to one or more of the groups on the crosslinking agent.

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Depending on the density of the cellulosic substrate, the substrate alone, such as a cotton carpet or raised surface and lightweight apparel, can be nearly fire resistant enough to meet the U.S. requirements for flammability. A small increase in fire resistance can be sufficient to meet the U.S. guidelines. Accordingly, the use of conventional fire retardants such as organophosphorous compounds, halogenated aromatics, and metal carbonates, which impart fire resistance but which each have inherent problems associated with their use, can be avoided.

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Definitions

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The following definitions are used herein:

The term "pill test" as used herein is a test used to determine whether a carpet is sufficiently fire resistant for use in the home. It calls for igniting a methenamine pill, which is placed in the center of a nine-inch by nine-inch carpet specimen. If the flame spreads to within one inch of a metal template
5 containing an eight-inch diameter hole, which is placed on top of the carpet specimen prior to igniting the pill, the specimen fails. If the flame does not spread to within one inch of the metal template, then the specimen passes. For a residential carpet, as described above, to be saleable, at least seven out of eight specimens must pass the test. Furthermore, if the carpet has been
10 treated with a flame-retardant (with the exception of alumina trihydrate added to the back coating), then the carpet must be washed ten times as described in AATCC 124-1967 prior to testing.

The term "45 degree angle test" as used herein refers to the
15 flammability test for wearing apparel outlined in the Code of Federal Regulations Title 16, Part 1610. This test method determines the flammability of fabrics with raised surface fibers such as fleece or light weight fabrics. It calls for placing the specimen to be tested at a 45 degree angle and igniting it by exposing the surface to an open flame for one
20 second. The flame must be one inch from the tip of the flame to the gas nozzle. The rate and intensity of the spread of the flame will categorize the flammability of the fabric.

The term "acceptable hand" as used herein refers to the feel of the
25 resulting substrate after it has been treated with the fire retardant composition.

The term "cellulosic substrate" as used herein refers to substrates that include cellulosic fibers, such as cotton, jute, flax, hemp, ramie, Lyocell,
30 Tencel®, regenerated unsubstituted wood celluloses such as rayon, blends thereof, and blends with other fibrous materials in which at least about 25

percent, preferably at least about 40 percent of the fibers are cellulosic materials. The term "fiber" relates to fibers present in a substrate such as a carpet, raised surface and lightweight apparel, upholstery, woven, knit, and nonwoven fabrics, and the like.

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The term "flame retardant" as used herein refers to the chemical applied to the cellulosic substrate. The term "flame resistant" refers to the treated cellulosic substrate. The terms "flame resistant" and "reduced flammability" as applied to substrates are not intended to imply that the materials are fireproof, or that they will not burn.

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The term "effective fire retardant amount" refers to an effective amount such that the treated substrate passes the required flammability test for that particular substrate.

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The term "degree of substitution" refers to the number of hydroxy groups in the cellulosic substrate which are esterified, on average, per glucose moiety. For example, fire resistance can be obtained by esterifying a relatively low number of hydroxy groups on average on the cellulosic substrate.

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The term "light weight fabrics" refers to fabrics with an area density of less than 2.6 ounces/square yard for general wearing apparel, as defined by the U.S. Code of Federal Regulations, 16 C.F.R. § 1610..

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I. The Fire Retardant Composition Used in Embodiment A

The fire-retardant composition includes a carboxylic acid-containing moiety, a suitable solvent, and, optionally, additional components which preferably do not interfere to a significant degree with the esterification chemistry.

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A. Carboxylic Acid-containing Moieties

Any aliphatic, alicyclic, or aromatic mono-, di-, tri- or polycarboxylic acid can be used which can covalently link to a cellulosic substrate when an aqueous solution of the acid is applied to the cellulosic substrate and the substrate is heated.

Preferably, in aliphatic polycarboxylic acids, each carboxyl group is two or three carbons away from another carboxyl group. Preferably, in aromatic polycarboxylic acids, each carboxyl group is ortho to another carboxylic group. In one embodiment, the compounds are C₂₋₂₀ straight, branched or cyclic di-, tri- or polycarboxylic acids, wherein an oxygen or sulfur atom is optionally present in one or more places on the molecule.

Examples of such compounds include maleic acid, malic acid, fumaric acid, tartaric acid, citric acid, citraconic acid, itaconic acid, tricarballic acid, trans-aconitic acid, 1,2,3,4-butanetetracarboxylic acid, all-cis-1,2,3,4-cyclopentane tetracarboxylic acid, mellitic acid, oxydisuccinic acid, thiodisuccinic acid, and the like, or anhydrides or acid halides of these acids. The preferred carboxylic acids are maleic acid, malic acid, succinic acid, tartaric acid, citric acid, and copolymers of maleic and acrylic acid.

In another embodiment, the compounds are polymers which include at least three carboxyl groups. Examples of such compounds include poly(methyl)maleic acid, carboxymethyl cellulose, poly(meth)acrylic acid, polymaleic acid, polyacrylic acid, copolymers and blends thereof, and anhydrides or acid halides of these acids. Also suitable are carboxymethyl cellulose fixed with an external crosslinker and gluconic acid fixed by an external crosslinker.

Preferably, the carboxylic acids include at least two carboxyl groups, so as to effectively bond to at least a portion of the hydroxy groups on the cellulosic material. However, the mechanism of flame resistance,

conceivably, is through the decarboxylation of the carboxylic acid during combustion. Some of the dicarboxylic acids also contain hydroxyl groups that may be released as water vapor during combustion. The acids may also promote char formation. Since the ester linkages appear to function by releasing carbon dioxide when the material catches fire, it can be sufficient to use monocarboxylic acids to achieve adequate fire resistance, alone or in combination with the di-, tri- and polycarboxylic acids.

The carboxylic acids can optionally include other reactive functional groups, for example, carbon-carbon double bonds, halides, amines, phosphorous esters, monosaccharides, disaccharides, polysaccharides, amides and imides. The presence of olefins can allow further crosslinking, and the presence of halides can provide additional fire resistance. Perfluoroalkyl and perfluoroaryl groups can impart stain resistant properties to the composition. Hydroxy groups, which can be present, may not be preferred as they may interfere with the desired coupling chemistry and also cause some yellowing in the treated fiber compositions.

B. Suitable Solvents

Preferably, the carboxylic acid is present in an aqueous solution, suspension or dispersion. However, other volatile solvents which are inert to the coupling chemistry and in which the carboxylic acid is soluble or uniformly dispersible can be used. The composition can be in the form of a solution or an emulsion.

C. Optional Components

Additional components can optionally be added to the fire-retardant composition. These include, but are not limited to, other fire retardants, dyes, wrinkle resist agents, de-foaming agents, buffers, pH stabilizers, fixing agents, stain repellents such as fluorocarbons, stain blocking agents, soil repellents, wetting agents, softeners, water repellents, stain release agents,

optical brighteners, emulsifiers, and surfactants.

Suitable additional fire retardants include, but are not limited to, metal oxides, metal carbonates, halocarbons, phosphorous esters, phosphorous amines, phosphorous-based acids, aluminum trihydrate, and nitrogen-containing compounds.

II. The Fire Retardant Composition Used in Embodiment B

The fire-retardant composition includes an amino acid, protein and/or peptide, and may also include a crosslinking agent and/or coupling agent, as well as various other optional components, along with a suitable solvent. In some embodiments, the amino acid, protein and/or peptide will be covalently linked to the cellulosic material. In other embodiments, it will not be covalently linked to the cellulosic material. In those embodiments in which crosslinking is desirable, it may be necessary to use a crosslinking or coupling agent.

A. Amino acids, Proteins and/or Peptides

Amino acids are organic acids containing both a basic amine group and an acidic carboxylic acid group. They are amphoteric and exist in aqueous solution as dipolar ions. There are twenty five naturally occurring amino acids that are the constituents of naturally occurring proteins and peptides. These naturally occurring amino acids have an amine group at a position alpha to the carboxylic acid group. However, non-naturally occurring amino acids can also be used in the compositions and methods described herein. Some amino acids include various functional groups, such as amine, thiol, hydroxy and carboxylic acid groups in addition to the amine and carboxylic acid groups that are present in all amino acids.

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Proteins and peptides are polymers formed by sequentially linking

various amino acids. The amine group of one amino acid and the carboxylic acid of the next amino acid are linked via an amide bond, also known as a peptide bond. Proteins are produced naturally, and can also be produced in protein synthesizers and by fermentation techniques. A difference between proteins and peptides is the size of the molecules. Peptides typically include between 2 and 100 amino acids, and proteins typically include more than 100 amino acids. There are numerous proteins and peptides, both naturally occurring and synthetic, all of which can be used. In some embodiments, the proteins are modified with reactive groups which enable the protein to be covalently linked to the cellulosic material without the need for an additional crosslinking or coupling agent. Such proteins can be preferred due to their relative ease of application.

Examples of proteins include vegetable proteins such as soy proteins, milk proteins such as casein, and enzymes.

Enzymes are very large, complex protein molecules consisting of intertwined chains of amino acids. They are formed within the cells of all living creatures, plants, fungi, bacteria, and microscopic single cell organisms. They are typically highly biodegradable and pose no threat to the environment.

Enzymes can be categorized according to the compounds they act upon. For example, lipases split fats into glycerol and fatty acids, catalases break down hydrogen peroxide, amylases break down starch into simple sugars, proteases break down proteins, cellulases break down cellulose, pectinases break down pectin, xylanases break down xylan, isomerases catalyze conversion of glucose to fructose, beta-glucanases break down beta-glucans, maltases convert maltose to glucose, trypsin splits proteins to amino acids, zymases convert sugar to alcohol and carbon dioxide.

Suitable enzymes include cellulases, lipases, catalases, amylases, proteases, pectinases, xylanases, isomerases, maltases, zymases, trypsin, endo glucanases, beta-glucanases and others which, when applied to a cellulosic material, provide the material with the desired level of fire
5 resistance for the intended application.

The enzymes described herein are either commercially available or can be prepared using known methodology. Enzymes are typically produced commercially by heating a fermentation broth under aseptic conditions to
10 form a completely sterile nutrient medium. The nutrient is converted into a desired enzyme by carefully selected microorganism action in the presence of oxygen. The choice of broth, microorganism, and operating conditions determine the type and yield of enzyme. Once fermentation is completed, various centrifugal, filtration, and precipitation processes separate the
15 enzyme from the fermentation broth.

The mechanism of flame resistance is believed to involve, in part, the decarboxylation of the carboxylic acid groups in the amino acids, proteins and/or peptides during combustion. Some of the amino acids in the amino
20 acids, proteins and/or peptides also contain hydroxyl groups that may be released as water vapor during combustion. The carboxylic acids may also promote char formation. The nitrogen contained in the amino acids, proteins or peptides may also serve to reduce the flammability of the substrate.

25 As the enzymes are prepared from amino acids, they include various reactive groups such as hydroxy groups, thiols, amines, and carboxylic acids. Carboxylic acids are known to react with hydroxy groups under various coupling conditions to form ester linkages. Thiols, amines and hydroxy groups on enzymes do not react directly with the hydroxy groups on the
30 cellulosic materials, but can be covalently linked via crosslinking agents.

B. Crosslinking Agents

The reactive groups (hydroxy, thiol, amine and carboxylic acid groups) on the amino acids, proteins and/or peptides can be covalently linked to the hydroxy groups on the cellulosic substrate by means of crosslinking agents.

Reactive functional groups which participate in nucleophilic substitution reactions are typically nucleophiles, i.e., amine, hydroxy, and thiol groups, or leaving groups, i.e., chlorides, tosylates, mesylates, and the like. Using nucleophilic substitution chemistry, one cannot directly link two nucleophiles or two leaving groups. However, it is possible to link nucleophilic groups on two molecules by reacting them with a single molecule which has two leaving groups, or a functional group capable of reacting with both nucleophiles. This type of molecule is known as a crosslinking agent. Crosslinking agents are well known to those of skill in the art.

Crosslinking agents can be used to covalently link thiol, amine, carboxyl and/or hydroxy group on the amino acids, proteins and/or peptides with the hydroxy groups on the cellulosic material. Preferably, a sufficient quantity of crosslinking agents is present to covalently link at least a sufficient amount of amino acid, protein and/or peptide to the cellulosic material to render it fire resistant enough for the intended use.

Some crosslinking agents include one functional group which is capable of reacting with two or more nucleophilic groups under appropriate conditions. Examples of these include ureas, carbonates, orthocarbonates, chloroformates, urethanes, phosgene, diphosgene, triphosgene, thiophosgene, and the like. Of these, ureas and other water-soluble crosslinking agents are preferred due to their relative ease of use and the avoidance of using organic solvents.

Other crosslinking agents include two or more functional groups which each are capable of reacting with one nucleophilic group. Examples include alkyl halides, alpha-halo carbonyl compounds such as acid halides, sulfonyl halides, anhydrides, esters, epoxides, oxiranes, divinyl sulfones, thioesters and the like. Examples of suitable dihalides include 1,2-dichloroethane, and 2,3-dichlorobutane. Examples of suitable diesters include dimethylsuccinate and dimethyl oxalate. Examples of suitable diacid halides include succinyl chloride and oxaloyl chloride.

Preferred crosslinking agents are water-soluble, and react with the cellulosic substrate under relatively mild conditions (i.e., temperatures less than about 200°C, pH between about 2 and 12, and do not contain appreciable amounts of formaldehyde or other materials known to be toxic to humans or animals on exposure. A preferred water-soluble crosslinking agent is a urea such as dimethyloldihydroxyethylene urea, imidazole, imidazolidinone, dialdehyde, and dichlorotriazine.

Dichlorotriazinyl compounds are well known to those of skill in the art, and have been used for years as crosslinking agents. Many of these compounds include carboxylic acid or sulfonic acid groups so that the compound is relatively water soluble at a certain pH range. An example of a suitable dichlorotriazinyl compound is N,N'-bis(dichloro-s-triazinyl)-4,4'-diaminostilbene-2,2'-disodiumsulphonate (T-DAS), which is well known to bond to cotton and also to amino, thiol and hydroxyl groups (see, for example, Lewis and Lao, "The use of a crosslinking agent to achieve covalent fixation of hydroxyethylsulphone dyes on cotton", AATCC 1998 International Conference and Exhibition, Philadelphia Marriott, Philadelphia, Pa, pages 375-383, (September 22-25, 1998), the contents of which are hereby incorporated by reference).

Dialdehydes are also well known to those of skill in the art, and have

been used for years to crosslink various compounds to proteins and peptides. Examples include C₂₋₆ dialdehydes, such as oxalaldehyde (Glyoxal), succindialdehyde and glutaraldehyde. They are typically sold as aqueous solutions, which are at least partially hydrated. Hydroxy groups are known to react with these compounds to form acetals and hemi-acetals. Amides, ureas and urethanes also react with dialdehydes to form various condensation products. Amines typically react with dialdehydes to form Schiff bases, which, if relatively unhindered, further react to form more complicated, uncharacterized products. The reaction with amide groups described above tends to proceed faster in alkaline media than in acidic media.

Imidazolidinones are commonly used in the textile industry. One example is dimethyloldihydroxyethylene urea (DMDHEU). DMDHEU is commercially prepared from glyoxal, urea and formaldehyde, and often contains residual formaldehyde. The presence of residual formaldehyde is not advantageous when contact of the treated cellulosic materials with animals or humans is anticipated.

There are several commercially available imidazole derivatives commonly used as crosslinking agents in the textile industry. These include the Fixapret™ family of crosslinking agents sold by BASF, including Fixapret NF™, which is commonly used with a catalyst system that includes a proprietary mixture of inorganic salts (Catalyst NB-202 from BASF).

Examples of suitable water-soluble crosslinking agents include Fixapret® NF (BASF) and Freerez® NFR (BF Goodrich).

C. Coupling Catalysts

One means for coupling amino acids, proteins and/or peptides to a cellulosic substrate without using crosslinking agents is to form ester linkages with the carboxylic acid groups on the amino acids, proteins and/or peptides and the hydroxy groups on the cellulosic substrate. Suitable coupling catalysts are well known to those of skill in the art. It may be necessary to protect groups on the amino acids, proteins and/or peptides that might interfere with the coupling chemistry, i.e., amine groups, if any, prior to forming the ester linkages.

10

There are several types of catalysts which can be used to esterify the carboxy groups on the amino acids, proteins and/or peptides with the hydroxy groups on the cellulosic materials. Examples of suitable catalysts include alkali metal salts of phosphorous-containing acids, including phosphorous acid, hypophosphorous acid, and polyphosphoric acid, and also include alkali metal mono and dihydrogen phosphates and hypophosphites. The most active catalysts of this type appear to be the alkali metal hypophosphites.

15

C. Suitable Solvents

Preferably, the amino acids, proteins and/or peptides, along with any suitable combination of crosslinking and/or coupling agents, are present in an aqueous solution, suspension or dispersion. However, other volatile solvents which are inert to the coupling chemistry and in which these materials are soluble or uniformly dispersible can be used.

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D. Optional Components

Additional components can optionally be added to the fire-retardant composition. These include, but are not limited to, other fire retardants, dyes, wrinkle resist agents, de-foaming agents, buffers, pH stabilizers, fixing agents, stain repellants such as fluorocarbons, stain blocking agents, soil

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repellants, wetting agents, softeners, water repellants, stain release agents, optical brighteners, emulsifiers, and surfactants.

5 In one embodiment, the cellulosic substrate is a carpet. When other fire retardants are used in carpets, they can be present in or on the carpet fiber or the backing material. Preferably, no formaldehyde or other volatile organic compounds are released from the backing layer. Further, the fire retardants are preferably compatible with any latex formulation used in the carpet backing.

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Suitable additional fire retardants include, but are not limited to, metal oxides, metal carbonates, halocarbons, phosphorous esters, phosphorous amines, phosphate salts, other phosphorus containing compounds, aluminum trihydrate, and nitrogen-containing compounds other than amino acids, proteins and/or peptides.

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III. The Fire Retardant Composition Used in Embodiment C

The fire-retardant composition includes a crosslinking agent, as well as various other optional components, along with a suitable solvent. The crosslinking agent is covalently linked to the cellulosic material.

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A. Crosslinking Agents

In this embodiment, suitable crosslinking agents include compounds with two or more reactive groups which are capable of reacting with the hydroxy groups on cellulosic materials, or reacting with tosylate, mesylate, triflate or other leaving groups prepared from the hydroxy groups on cellulosic materials. Suitable crosslinking agents include those described above in Embodiment B.

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30 In this embodiment, crosslinking agents are used to covalently crosslink the hydroxy groups on the cellulosic material. Preferably, a

sufficient quantity of crosslinking agents is present to covalently crosslink at least a sufficient amount of hydroxy groups on the cellulosic material to render it fire resistant enough for the intended use. For cotton carpets, a sufficient amount of crosslinking is typically between 0.12 and 2.0 percent of the hydroxy groups on the cotton.

B. Phosphorus-Based Compounds

The crosslinking agents which crosslink the cellulosic substrate can also crosslink the substrate with phosphorus-based compounds. As used herein, "phosphorus-based compounds" are compounds which include a phosphorus atom and which are capable of being covalently linked to a crosslinking agent and/or a cellulosic substrate. Numerous phosphorus-based compounds are known for their fire retardant properties. Any phosphorus-based compound which is capable of being crosslinked with a cellulosic substrate via a crosslinking agent as defined herein can be used.

Preferably, the phosphorus-based compounds include one or more reactive groups which can react with the crosslinking agent. Examples of suitable groups include halogen, hydroxy, carboxylic acid, aldehyde and amide groups. Suitable phosphorus-based acids include phosphorus acid, hypophosphorus acid, and polyphosphoric acid, and also include alkali metal mono and dihydrogen phosphates and hypophosphites. Examples of other suitable phosphorus-based compounds include (di) phosphonium halide, dialkyl 1-amino-1-deoxyglucityl phosphonates, phosphorus amides, amino polyhydroxyalkyl phosphonic acid, phosphonitrile chloride, phosphorimidic chloride, tris(haloalkyl) phosphates, haloalkyl phosphates, dihydroxyalkyl phosphite, dialkylphosphonoalkane amide, bis(haloalkyl) haloalkyl phosphonate, (mercapto)phosphonitrilate, N-hydroxyalkyl phosphonic esters, bis-(hydroxyalkyl)-phosphinic acid, tetrakis (α -hydroxyalkyl) phosphonium halide, aryl haloalkyl phosphonate, hydroxyalkyl phosphonium salts, tris(polyhaloaryl) phosphate, halogenated phosphorthioates, phosphorus

polyamides, phosphonitrilic halides, bis-(hydroxypolyalkoxyalkyl aminoethyl) phosphonates, where polyalkoxy is haloalkyl substituted, amino epoxy phosphonates and n-substituted derivative including polyphosphonates, N-hydroxymethyl-3-phosphonopropionamide, haloalkyl or hydroxyalkyl-allyl-phosphonium halide, haloalkylphosphine oxide
5 haloalkylphosphinic acids, tetrahydroxydiphosphorinane dioxide, tris(2-chloroethyl phosphate), tris(1-chloro-2-propyl) phosphate, tris (1,3-dichloro-2-propyl) phosphate, 2-bromoethyl-2-chloroethyl 3-bromopentyl phosphate, tetrakis (2-chloroethyl)ethylene diphosphate, bis(2-chloroethyl) 2-chloroethyl
10 phosphonate, oligomeric phosphonate-phosphate, oligomeric chloroethyl ethylene phosphate tris(3-hydroxypropyl) phosphine oxide, isobutylbis(3-hydroxypropyl) phosphine oxide, and bis(2-chloroethyl) vinyl phosphonate.

In a preferred embodiment, the phosphorus based compound is fixed
15 onto the cellulosic substrate by reaction with maleic acid or another dicarboxylic or polycarboxylic acid and sodium phosphate, or sodium hypophosphite.

As used herein, the term "alkyl" refers to monovalent straight,
20 branched or cyclic alkyl groups preferably having from 1 to 20 carbon atoms, more preferably 1 to 10 carbon atoms ("lower alkyl") and most preferably 1 to 6 carbon atoms. This term is exemplified by groups such as methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *iso*-butyl, *n*-hexyl, and the like. In those cases where the minimum number of carbons are greater than one, *e.g.*, alkenyl
25 (minimum of two carbons) and cycloalkyl (minimum of three carbons), it is to be understood that "lower" means at least the minimum number of carbons.

As used herein, the term "aryl" refers to an unsaturated aromatic
30 carbocyclic group of from 6 to 14 carbon atoms having a single ring (*e.g.*, phenyl) or multiple condensed (fused) rings (*e.g.*, naphthyl or anthryl).

Preferred aryls include phenyl, naphthyl and the like. Unless otherwise constrained by the definition for the aryl substituent, such aryl groups can optionally be substituted with from 1 to 5 substituents and preferably 1 to 3 substituents selected from the group consisting of hydroxy, acyl, alkyl, alkoxy, alkenyl, alkynyl, substituted alkyl, substituted alkoxy, substituted alkenyl, substituted alkynyl, amino, substituted amino, aminoacyl, acyloxy, acylamino, alkaryl, aryl, aryloxy, azido, carboxyl, carboxylalkyl, cyano, halo, nitro, heteroaryl, heteroaryloxy, heterocyclic, heterocycloxy, aminoacyloxy, oxyacylamino, thioalkoxy, substituted thioalkoxy, thioaryloxy, thioheteroaryloxy, and trihalomethyl. Preferred substituents include alkyl, alkoxy, halo, cyano, nitro, and trihalomethyl.

As used herein, the terms "halo" or "halogen" refer to fluoro, chloro, bromo and iodo and preferably is either bromo or chloro. The terms haloalkyl and haloaryl refer to alkyl and aryl groups substituted with between 1 and 5, preferably between 1 and 3 halogen groups.

The phosphorus-based compounds are preferably linked to the crosslinking agent, which is in turn crosslinked with the cellulosic substrate. Means for linking the phosphorus-based compounds and crosslinking agents described herein are well known to those of skill in the art.

In one embodiment, the phosphorus-based compounds are coupled via a crosslinking agent to a cellulosic substrate by forming phosphate ester linkages with the phosphoric acid groups on the phosphorus-based compounds and a first reactive group on the crosslinking agent, and a second reactive group on the crosslinking agent is then reacted with the cellulosic substrate.

In those embodiments in which phosphorus based compounds are used, the resulting cellulosic substrate can be fire retardant enough for use in

end uses requiring flame-retardant finishes. Examples of such end uses include protective clothing (e.g., foundry workers apparel and fire fighters uniforms), children's sleepwear, furnishing/upholstery, bedding, carpets, curtains/drapes, and tents.

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For all of these fabric end uses, the chemicals can be applied, for example, by padding at 50-150 percent wet pickup, preferably between 70 and 100 percent wet pickup. However, other application techniques can also be used.

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C. Suitable Solvents

Preferably, the crosslinking agents, along with any phosphorus-based compounds, are present in an aqueous solution, suspension or dispersion. However, other volatile solvents which are inert to the coupling chemistry and in which these materials are soluble or uniformly dispersible can be used.

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D. Optional Components

Additional components can optionally be added to the fire-retardant composition. These include, but are not limited to, other fire retardants, dyes, wrinkle resist agents, de-foaming agents, buffers, pH stabilizers, fixing agents, stain repellants such as fluorocarbons, stain blocking agents, soil repellants, wetting agents, softeners, water repellants, stain release agents, optical brighteners, emulsifiers, and surfactants.

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In one embodiment, the cellulosic substrate is a carpet. When other fire retardants are used in carpets, they can be present in or on the carpet fiber or the backing material. If a fire retardant is present in the backing layer, the fire retardant is preferably a material that activates at a temperature lower than alumina trihydrate. Preferably, no formaldehyde or other volatile organic compounds are released from the backing layer. Further, the fire

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retardants are preferably compatible with any latex formulation used in the carpet backing.

Suitable additional fire retardants include, but are not limited to,
5 metal oxides, metal carbonates, halocarbons, phosphorus esters, phosphorus amines, phosphate salts, other phosphorus containing compounds, aluminum trihydrate, and nitrogen-containing compounds.

IV. Cellulosic Substrates

10 Any cellulosic substrate which includes hydroxy groups can be treated with the above compositions. Cotton is a preferred cellulosic fiber. Other cellulosic fibers include flax, jute, hemp, Tencel®, Lyocell, ramie and regenerated unsubstituted wood celluloses such as rayon. The material can be a blend of fibers, such as a blend of cotton and a polyolefin such as
15 polypropylene, a polyester or polytrimethyl terephthalate (PTT). The fiber composition is preferably at least 25, and, more preferably, at least 40 percent by weight cotton.

Any area density of carpet, raised surface and lightweight apparel, or
20 other woven, knit or nonwoven fabrics, can be constructed and used which is practical from a manufacturing standpoint.

V. Articles of Manufacture Prepared from the Composition

The treated fiber compositions can be used for several purposes,
25 including cotton carpets, raised surface and lightweight apparel, articles of clothing, etc. Cotton carpets are a preferred article of manufacture. Raised surface and lightweight apparel are also preferred articles of manufacture. When used in carpets, the yarn in the carpet has an area density of between 20 oz/yd² and 120 oz/yd², more preferably between 30 oz/yd² and 80 oz/yd².

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VI. Methods of Manufacturing the Fire Retardant Compositions

The compositions described herein are either commercially available or can be prepared using known methodology. They can be added to a desired solvent at a desired amount to form a desired concentration and form a fire retardant solution.

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VII. Methods of Treating the Cellulosic Substrate

The methods described herein involve adding one or more of the fire retardant compositions described herein to a cellulosic substrate, and reacting the composition with the substrate.

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The solutions including the fire retardant compositions described herein are added in any suitable proportion, but preferably, the amount of the solution is between 1.0 and 200 percent by weight of the fiber to be treated, more preferably, between 5.0 and 100 percent by weight, and most preferably, between about 15 and 80 percent.

15

The above ranges vary depending on the mode of application and the cellulosic substrate to be treated. For example, when the composition is applied by spray, foam or other low wet pickup methods commonly used for treating carpets with fluorochemicals, the percent by weight of the fire retardant solution which is applied to the cellulosic substrate is typically between 5 and 100 percent by weight, preferably between about 10 and 50 percent by weight, and more preferably, between about 15 and 30 percent by weight of the fiber to be treated.

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For raised surface and lightweight apparel, larger amounts of the fire retardant solution may be required to achieve adequate fire resistance. The same general principal, of adjusting the solution concentration based on the total wet add-on, applies to other substrates as well, such as fiber fill, upholstery, children's sleepwear, bedding, batting, protecting clothing and drapes.

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An amount of about 15 percent by weight of bath on carpet is particularly well suited for spray application, foam application or other low, wet pickup methods commonly used for treating carpets with fluorochemicals. The use of these methods and types of solutions helps to avoid adding excess water which will have to be removed during drying.

After the composition is applied and excess water is removed, the material is typically heated at a sufficient temperature and for a sufficient time to drive off the solvent and/or react at least a portion of the functional (reactive) groups in the fire retardant composition with the groups on the cellulosic substrate. For example, in Embodiment A, and with some crosslinking agents in Embodiments B and C, all or a portion of the hydroxy groups on the material are esterified. With respect to Embodiment C, functional (reactive) groups on the fire retardant composition optionally also react with the phosphorus-based compound. The material can then optionally be rinsed to remove residual, unreacted chemicals, and then dried.

For carpets, there are a variety of application techniques which can be used to apply the fire retardant solutions. These include spray, foam, immersion, dipping, dripping, cascading, liquor circulation throughout the substrate, padding, kiss rolls, and doctor blades. These techniques may be used alone or in conjunction with vacuum, squeeze rolls, centrifuge, air knives, gravity drainage or other techniques. The application can be done via a continuous or batch method.

The composition can also be applied by other application techniques, including by exhaust application. In an exhaust application the liquor ratio may vary over a broad range of about 2 to 1 up to about 50 to 1. More preferably about 3 to 1 to about 20 to 1, meaning about 20 pounds of treating solution per pound of cellulosic containing substrate. In one preferred embodiment the liquor ratio is about 10 to 1 and the concentration of the

crosslinking agent is adjusted accordingly down to a concentration ranging from 0.001 percent to about 5.0 percent and preferably from about 0.01 to 1.0 percent on the weight of the treating liquor which is equivalent to 0.1 percent to 10.0 percent on the weight of the cellulosic substrate. With respect to Embodiments B and C, wet crosslinking agents, which can also be applied by exhaust techniques from the same bath, can be applied with phosphorus-based compounds to provide covalent linkages which result in treatments which are durable to various cleaning techniques. One such wet crosslinking agent is known as T-DAS, a dichlorotriazine crosslinking agent.

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As with the spray and foam application described above, the crosslinking reaction can occur in the dry state after the excess water has been removed or in the wet state, before the excess water is removed.

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The application(s) of the fire retardant solutions may be done to the fiber, yarn or carpet, either before, after, or in conjunction with other manufacturing or processing steps, such as dyeing, winding, cabling, heat setting, tufting, knitting or weaving.

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For raised surface and lightweight apparel, or any other apparel that may benefit from a reduction in flammability, the application may be done by any of the above mentioned techniques in fiber, yarn, fabric or garment form. Spraying, de-foaming, dipping or the "Metered Addition Process" are particularly suitable for garment application. The total amount of solution added to the substrate and the required concentration of reactive components, for example, carboxylic acids, amino acids, proteins, peptides, crosslinking agents and phosphorus-based compounds, in the solution will be dependent on many factors including the flammability test method, the weight and construction of the substrate, and blend levels of the many possible fibers in a blend.

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Suitable reaction times are typically between approximately one minute and five hours. However, the reaction times relate in part to the pH of the fire retardant solution and, with respect to embodiment A, the pKa of the particular carboxylic acid used. At a pH less than 11 for hydroxy, thiol and amine groups, or greater than 4 for carboxylic acids such as maleic acid, cure times are generally longer. However, there appears to be less of a change in the dye shade of dyed carpets when a pH greater than 4 is used.

Carpets typically have a polypropylene backing layer, which tends to melt or shrink at temperatures above 150°C. For this reason, it is preferable that this temperature not be exceeded when this type of carpet is treated. However, raised surface and lightweight apparel, upholstery, fiber fill, and carpets with non-thermoplastic backings may not have this type of temperature limitation. When these types of substrates are treated, the reaction temperature may be elevated as required, consistent with the scorching and/or yellowing temperature of these materials. One of skill in the art can readily determine an appropriate set of temperatures for a particular substrate to be treated.

Those of skill in the art can readily determine an appropriate set of reaction conditions (amount of fire retardant solution to add and suitable temperatures and reaction times) to form appropriate linkages, for example, in Embodiment A, ester linkages, between the cellulosic substrate and the fire retardant composition.

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Embodiment A

With respect to Embodiment A, at least a portion of the hydroxy groups on the cellulosic substrate and at least a portion of the carboxylic acid groups on the acid are covalently linked in an esterification reaction. The esterification conditions involve applying an appropriate amount of the composition to a cellulosic substrate and heating the substrate to a sufficient

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temperature for a sufficient time to crosslink an effective amount of the hydroxy groups on the cellulosic substrate to impart adequate fire retardance for the intended use of the substrate.

5 Preferably, the substrate is heated to a temperature between about 100 and 200°C for between 15 and 30 minutes. While not desiring to be limited to a particular theory, it is believed that the chemistry involves the *in situ* production of anhydrides, which then react with the hydroxy groups on the cellulosic substrate. *In situ* production of anhydrides from an aqueous
10 solution of carboxylic acids is preferable to using anhydrides in a non-aqueous solution, since it avoids the use of non-aqueous solvents.

 Since the carboxylic acids used typically do not provide the carpet with odor or toxicity, subsequent rinsing may not be desired. Further, any
15 unreacted carboxylic acid or other functional groups may be used to attach other types of molecules, for example, via the formation of ester or amide linkages. Since phosphorous-based catalysts are not present, the amount of esterification is low relative to when phosphorous-based catalysts are used. This is advantageous, since only a relatively low degree of esterification is
20 required to render cellulosic materials fire resistant, whereas a relatively high degree of esterification is required to render the materials wrinkle resistant.

 The concentration of carboxylic acid required to be effective, based on both the weight of the solution and on the weight of the substrate, will be
25 dependent on the factors mentioned above for all substrates including raised surface and lightweight apparel, carpets, upholstery, and any other substrate where it is desirable to reduce the flammability. Any of the application techniques which are mentioned above, or which are used to apply other chemical treatments to fibrous substrates, are considered suitable to be used
30 herein for any cellulosic substrate where it is desired to reduce the flammability.

Where liquor ratios of the treating bath or solution are greater than 1:1 (i.e., greater than one pound of treating solution per pound of substrate), pre-treatment techniques, such as cationic pre-treatments can be used to encourage the treatment chemicals, for example: carboxylic acids, to exhaust
5 or move out of the solution and onto the cellulosic substrate.

Although the temperature required to effectively form the ester linkages would be expected to vary somewhat depending on the nature of the substrate to be treated and the anhydride, a typical range of temperatures is
10 between about 100 and 240°C, more preferably between 110 and 200°C. The temperature is preferably less than would otherwise be required to scorch the substrate. Excessive heating can cause yellowing of the substrate fibers, so care should be taken to control the reaction temperatures.

15 In those embodiments in which the carboxylic acid-containing compound includes carbon-carbon double bonds, these bonds can be polymerized before, simultaneous with, or after forming the ester linkages with the hydroxy groups on the cellulosic substrate. Methods for polymerizing carbon-carbon double bonds are well known to those of skill in
20 the art, and typically involve the addition of a free radical polymerization initiator, such as t-butyl peroxide, persulfates, or azobisisobutyronitrile (AIBN).

Embodiment B

25 With respect to Embodiment B, at least a portion of the hydroxy groups on the cellulosic substrate and at least a portion of the reactive functional groups on the amino acid, protein and/or peptide and the crosslinking agent are covalently linked. The reaction conditions involve applying an appropriate amount of the composition to a cellulosic substrate
30 and heating the substrate to a sufficient temperature for a sufficient time to crosslink an effective amount of the hydroxy groups on the cellulosic

substrate to impart adequate fire retardance for the intended use of the substrate.

5 Methods for covalently linking a hydroxy group such as those on a cellulosic substrate and a hydroxy, thiol, amine or carboxyl group such as those on an enzyme are well known to those of skill in the art. Conventional means involve using crosslinking agents, preferably those that do not contain formaldehyde or other toxic substances. Preferred methods are those which can be performed in aqueous solvents.

10

In one embodiment, the amino acids, proteins and/or peptides are applied by exhaust application. In an exhaust application the liquor ratio may vary over a broad range of about 2 to 1 up to about 50 to 1. More preferably about 3 to 1 to about 20 to 1, meaning about 20 pounds
15 of treating solution per pound of cellulosic containing substrate. In one preferred embodiment the liquor ratio is about 10 to 1 and the amino acid, protein and/or peptide concentration is adjusted accordingly down to a concentration ranging from 0.001 percent to about 5.0 percent and preferably from about 0.01 to 1.0 percent on the weight of the treating liquor which is
20 equivalent to 0.1 percent to 10.0 percent on the weight of the cellulosic substrate.

Any unreacted functional groups on the amino acids, proteins and/or peptides, such as hydroxy, thiol, amine or carboxylic acid groups, may be
25 used to attach other types of molecules, for example, via the formation of ester or amide linkages.

Where liquor ratios of the treating bath or solution are greater than 1:1 (i.e., greater than one pound of treating solution per pound of substrate),
30 pre-treatment techniques, such as cationic pre-treatments can be used to encourage the treatment chemicals, for example, the crosslinking and/or

coupling agents, to exhaust or move out of the solution and onto the cellulosic substrate.

Although the temperature required to effectively form the linkages would be expected to vary somewhat depending on the nature of the substrate to be treated and the amino acid, protein and/or peptide, a typical range of temperatures is between about 20 and 240°C, more preferably between 40 and 200°C. The temperature is preferably less than would otherwise be required to scorch the substrate. Excessive heating can cause yellowing of the substrate fibers, so care should be taken to control the reaction temperatures. Coupling and/or crosslinking agents which will react with both the amino acid, protein and/or peptide and the cellulosic material in the wet state can be used to achieve fixation or reaction in the dyeing equipment used to dye cellulosic substrates.

15

It can be difficult to prepare anhydrides *in situ* when amino acids, proteins and/or peptides containing only one carboxylic acid group are used. For these materials, it may be desirable to use conventional chemistry, such as the formation of acid halides or anhydrides and application of these materials to the carpet, rather than forming anhydrides *in situ*.

20

Embodiment C

With respect to Embodiment C, at least a portion of the hydroxy groups on the cellulosic substrate and at least a portion of the reactive functional groups on the crosslinking agent are covalently linked. The reaction conditions involve applying an appropriate amount of the composition to a cellulosic substrate and heating the substrate to a sufficient temperature for a sufficient time to crosslink an effective amount of the hydroxy groups on the cellulosic substrate to impart adequate fire retardance for the intended use of the substrate.

25
30

Methods for covalently linking a hydroxy group such as those on a cellulosic substrate and a reactive groups present on a crosslinking agent are well known to those of skill in the art. Preferably, the crosslinking agents do not contain formaldehyde or other toxic substances. Preferred methods are those which can be performed in aqueous solvents.

The material can then optionally be rinsed to remove residual, unreacted chemicals, and then dried. However, since the crosslinking agents used typically do not provide the carpet with odor or toxicity, subsequent rinsing may not be desired. Further, any unreacted functional groups on the crosslinking agents may be used to attach other types of molecules, for example, via the formation of ester or amide linkages. Examples of such molecules include fluoroalkyl compounds commonly used to impart stain-resist properties to carpets and other textile goods.

The concentration of crosslinking agent(s) required to be effective, based on both the weight of the solution and on the weight of the substrate, will be dependent on the factors mentioned above for all substrates including raised surface and lightweight apparel, carpets, upholstery, and any other substrate where it is desirable to reduce the flammability. Any of the application techniques which are mentioned above, or which are used to apply other chemical treatments to fibrous substrates, are considered suitable to be used herein for any cellulosic substrate where it is desired to reduce the flammability.

Where liquor ratios of the treating bath or solution are greater than 1:1 (i.e., greater than one pound of treating solution per pound of substrate), pre-treatment techniques, such as cationic pre-treatments can be used to encourage the treatment chemicals, for example, the crosslinking agents and/or phosphorus based compounds, to exhaust or move out of the solution and onto the cellulosic substrate.

Although the temperature required to effectively form the linkages would be expected to vary somewhat depending on the nature of the substrate to be treated and the crosslinking agent(s), a typical range of temperatures is between about 20 and 240°C, more preferably between 40 and 200°C. The temperature is preferably less than would otherwise be required to scorch or melt thermoplastic components of the substrate. Excessive heating can cause yellowing of the substrate fibers, so care should be taken to control the reaction temperatures. Crosslinking agents which will react with the cellulosic material, and, optionally, the phosphorus-based compound, in the wet state can be used to achieve fixation or reaction in the dyeing equipment used to dye cellulosic substrates.

The fire retardant compositions in Embodiments C can also be used to prepare protective clothing (e.g., foundry workers apparel and fire fighters uniforms), children's sleepwear, furnishing/upholstery, bedding, carpets, curtains/drapes, and tents. There are a variety of application techniques which can be used to apply the fire retardant solutions to these substrates. These include immersion, dipping, dripping, cascading, liquor circulation throughout the substrate, padding, kiss rolls, and doctor blades. These techniques may be used alone or in conjunction with vacuum, squeeze rolls, centrifuge, air knives, gravity drainage or other techniques. The application can be done via a continuous or batch method.

VIII. Methods of Evaluating the Fire Retardant Cellulosic Compositions

The suitability of the fire retardant composition for an intended use will depend on the ability of the treated cellulosic substrate to pass various standard flammability tests. The currently accepted test for carpets is the pill test. The currently accepted test for raised surface apparel is the 45 degree angle test.

The testing protocol for these tests is well known to those of skill in the art. Using these tests, with a suitably prepared reduced flammability cellulosic fiber composition, one can readily determine the efficacy of the fire retardant composition for its intended use.

5

The present invention will be further understood with reference to the following non-limiting examples.

10

Example 1: Use of Maleic Acid without Phosphorus-Based Catalysts to Reduce Carpet Flammability

The purpose of this experiment was to ascertain whether maleic acid without a phosphorus catalyst will provide enough flame retardancy to allow cotton carpets to pass the pill test.

15

Carpet samples treated with maleic acid without a catalyst or with sodium hydroxide passed the pill test after 10 home launderings (HL). When potassium acetate was used to catalyze the reaction, flammability results were only marginal, i.e., one sample passed and one failed. The same marginal result was noted when a non-formaldehyde resin (Freerez NFR, Freedom) was applied to attempt to crosslink the acid to cotton. Sodium bicarbonate did not work as a catalyst for this reaction.

20

Experimental Approach:

25

Aqueous solutions of maleic acid, with or without added catalyst, were sprayed onto wet-on-dry onto carpet CD98-054-1 (75% cotton/25% bicomponent polyester, 1/8 inch gauge, 9 stitches per inch (spi), 21/32-inch cut pile) (40 ounces/square yard) at 15% target add-on. Bicomponent polyester is a sheath/core fiber with low melt polyester as the sheath and "regular" polyester as the core.

30

Two series of experiments were run, series 55 and series 65. The

amount of maleic acid and catalyst which was sprayed onto the carpet is shown in Table I. In series 55, fluorochemical (Scotchgard FX-1367, 3M) (5% on weight of bath ("owb")) and wetting agent (Alkanol 6112, Ciba Specialty Chemicals) (0.2% owb) were included in all baths except the control (water). In series 65, only wetting agent (0.2% owb) was included in the baths, except 65/6, which was a control. Sodium perborate (2% owb) was added to 65/2 to improve whiteness.

All samples were dried at 220°F (104°C) for 25 minutes. Specimens 55/1-3 and 65/1A were cured for 5 minutes at 280°F (138°C). The remaining pieces were cured at 250°F (121°C) for 5 minutes.

TABLE I

Treatment Formulations

Concentrations are given as % on weight of liquor

Sample	% Maleic acid	Catalyst	% Catalyst	Actual conc. acid % (owc ¹)	Actual % Liquor add-on
55/1	5	None	0.0	0.80	15.9
55/2	5	NaHCO ₃	3.0	1.24	24.9
55/3	0	None	0.0	0.00	0.0
65/1	5	None	0.0	0.73	14.6
65/2	5	None	0.0	0.77	15.4
65/3	5	NaOH	0.5	0.81	16.2
65/4	5	CH ₃ CO ₂ K	2.0	0.99	19.8
65/5	5	Resin + MgCl ₂	5.0	0.71	14.2
65/6	0	None	0.0	0.00	0.0

¹ owc = on weight of carpet.

Results and Discussion

After 10 home launderings (HL), two 5-inch x 5-inch specimens from each of the runs were pill tested, with the exception of run 65/2, which had four specimens tested. The pill test was conducted according to the Code of Federal Regulations (CFR) title 16, part 1630 test method (Code of Federal Regulations, Title 16 Part 1630, p. 632 (1995)).

The results given in Table II demonstrate that, in series 55, the sample treated with maleic acid and no catalyst had two specimens pass the pill test. However, some yellowing and stiffness was present. In order to overcome the yellowing, sodium perborate was added to the maleic acid solution (65/2) to act as a whitening agent. All four of those specimens and two others (65/1B) that were cured at the same temperature passed the pill test. A lower cure temperature was chosen as another means to reduce yellowing. There was no significant difference in color between the samples with perborate in the formulation and those without perborate. All of these samples had only a very slight color change from the control. The specimen, 65/1A, which was cured at 280°F (138°C) also had an acceptable color.

The solution used to treat sample 55/2 included bicarbonate, and exhibited effervescence due to breakdown to CO₂ while the solution was being mixed. This sample failed the pill test. Using potassium acetate as a catalyst only worked marginally. The amount of potassium acetate that was used in 65/4 brought the solution pH to 2.0. As pH increases, the acid groups are converted to carboxylate (salt) groups that are less reactive. The pH of 65/3, using NaOH as catalyst, was 1.7. Both specimens of 65/3 passed the pill test. Although the NaOH converted some of the maleic acid to sodium maleate, enough acid groups remained to react with the carpet. Incorporating resin into the finish to fix the flame retardant to the cotton was not successful.

TABLE II
Appearance and Flammability Test Results

	Sample	Odor	Hand	Yellowing	Before wash ¹ Pill Test	After 10 HL Pill Test
5	55/1	No	Slight stiffness	Slight	Pass	Pass
	55/2	No	Slight stiffness	No	Fail	Fail
	55/3	No	Soft	No	Fail	Fail
	65/1A	No	Soft	No	NT	1P/1F
	65/1B	No	Soft	No	1P/1F	Pass
10	65/2	No	Soft	No	Pass	Pass
	65/3	No	Soft	No	Pass	Pass
	65/4	No	Soft	No	Pass	1P/1F
	65/5	No	Soft	No	Pass	1P/1F
	65/6	No	Soft	No	Fail	Fail

15 ¹ Pass = both specimens passed. Fail = both specimens failed. 1P/1F
= 1 passed and 1 failed. NT= not tested.

Conclusions

20 Sodium bicarbonate and potassium acetate were not good catalysts
for the reaction of maleic acid with cotton. The absence of catalyst and a
catalytic amount of sodium hydroxide worked equally well to produce
carpets that passed the pill test.

25 Example 2: Evaluation of Crosslinkers for Fixing (Bonding) a Phosphorus-Based Flame Retardant (FR) at a Low Curing Temperature

Summary

30 Two modified ethylene urea-type (EU) resins yielded a reasonable
fixation of the phosphorus-based FR agent onto cotton carpets. The percent
fixation after ten (10) home launderings was in the same range as the original
reactive, phosphorus-based FR agent.

Introduction

A phosphorus-containing finish (FR) can provide reduced flammability of cotton carpets. In order to make this finish durable to the ten
5 laundryings required by federal regulations, a crosslinker was used to attach
this FR finish to the cotton.

Objective

10 Curing time was evaluated with one crosslinking resin. Several
resins were applied under the same curing conditions to compare the
effectiveness of each as a crosslinker for the FR.

Experimental Approach

15 TABLE III displays the formulations which were sprayed onto the
90/10 cotton/Foss low-melt polyester carpet CD-98-026 (cut pile, 1/8 inch
gauge, 9 stitches per inch (SPI), 21/32 inch pile height, 40 ounces/square
yard) at 15% target add-on. Actual application levels are given in TABLE
20 IV. All specimens were dried at 220°F (104°C) for fifteen minutes.
Samples 1 and 5 were cured for five minutes at 250°F, while the remaining
samples (2-4 and 6-8) were cured for 20 minutes at the same temperature.
Pill tests were performed on two 5 inch x 5 inch pieces before laundering
(HLTD), after 1 HLTD and after 10 HLTD. Phosphorus (P) analysis was
25 done by ICP-OES at Galbraith Laboratories.

TABLE III

Formulations

(Concentrations are given as % on weight of liquor)

30

	#	FR	Resin Type	% Resin	Catalyst	% Catalyst	Fluoro-chemical	Water
5	5/1	10	PCA	10	NaH ₂ PO ₂	5	5	70
	5/2	10	PCA	10	NaH ₂ PO ₂	5	5	70
	5/3	10	EU1	10	Catalyst (1)	2	5	73
	5/4	10	EU2	10	Catalyst (2)	5	5	70
	5/5	5	PCA	5	NaH ₂ PO ₂	5	5	80
	5/6	5	PCA	5	NaH ₂ PO ₂	5	5	80
	5/7 ¹	5	0	0	Catalyst (3)	5	5	85
10	5/8	0	0	0	0	0	0	100

¹Sample 7 contained the standard FR (control).

TABLE IV

Target and Actual Carpet Weights and Application Levels (% add-on)

Carpet Sample	Initial Dry wt. (g)	Target wt. (after spray) (g)	Actual wt. (after spray) (g)	Actual % add-on	Target conc. % owc FR/resin	Actual conc. % owc FR/resin
5/1	211.57	243.31	244.47	15.6	1.50/1.50	1.56/1.56
5/2	212.31	244.16	244.83	15.3	1.50/1.50	1.53/1.53
5/3	206.47	237.44	243.34	17.9	1.50/1.50	1.79/1.79
5/4	207.64	238.79	247.62	19.3	1.50/1.50	1.93/1.93
5/5	200.21	230.24	232.36	16.1	0.75/0.75	0.81/0.81
5/6	205.19	235.97	236.41	15.2	0.75/0.75	0.76/0.76
5/7	207.44	238.56	242.34	16.8	0.75/0.00	0.84/0.00
5/8	184.63	212.32	211.69	14.7	0.00/0.00	0.00/0.00

*owc = On Weight of Carpet

Results and Discussion

As the results in TABLES V and VI indicate, the samples that were cured for a longer time and were treated with higher concentrations of FR and crosslinker had poorer hand than the control samples. Curing for a shorter time can produce acceptable hand. At a FR/crosslinker concentration

of 1.50/1.50 % owc, all samples passed the pill test, even after 10 home launderings.

TABLE V

5 **Appearance and Flammability Test Results**

10

15

Sample	Odor	Hand	Yellowing	Before wash ¹ Pill Test	After 1 HL ¹ Pill Test	After 10 HL ¹ Pill Test
5/1	Slight	Soft	No	Pass	Pass	Pass
5/2	No	Fair	No	Pass	Pass	Pass
5/3	Very Slight	Fair	No	Pass	Pass	Pass
5/4	No	Fair	No	Pass	Pass	Pass
5/5	No	Soft	No	Pass	Fail	Pass
5/6	No	Fair	No	Pass	1P/1F	1P/1F
5/7	No	Soft	No	Pass	Pass	Pass
5/8	No	Soft	No	Fail	Fail	Pass

¹Pass = both specimens passed. Fail = both specimens failed. 1P/1F = 1 passed and 1 failed. HL = Home Launder.

20 Modified EU-type resins are preferred over PCA resins for crosslinking the FR.

TABLE VI
Phosphorus Analysis Results

	Sample	Avg. P (%) Before wash	Avg. P (%) After 1 HLTD	Avg. P (%) After 10 HL	Avg. % fixation after 10 HL
5	5/1	0.50	0.04	0.02	4
	5/2	0.64	0.09	0.05	8
	5/3	0.28	0.10	0.11	39
	5/4	0.48	0.22	0.13	27
	5/5	0.28	0.12	0.01	4
10	5/6	0.71	0.02	0.02	3
	5/7	0.16	0.10	0.05	31
	5/8	33 ppm	18 ppm	20 ppm	0

The FR agent, in conjunction with crosslinking chemistry is effective
 15 at reducing the flammability of cotton carpet.

Product Identification

Generic Name	Product Name	Supplier
	NaH_2PO_2	OxyChem
Catalyst (1)	Freecat LF	Freedom Textile Chemical
Catalyst (2)	NB-202	BASF
Catalyst (3)	Catalyst 531	Sequa Chemicals
Flurochemical	Scotchgard FX-1367	3M
FR	hydroxy-containing oligophosphate	Various suppliers
FR (control)	Pyrovatex CP new	Ciba Specialty Chemicals
PCA resin	polymaleic acid	Various suppliers
EU1	Freerez NFR	Freedom Textile Chemical
EU2	Fixapret NF	BASF

Modifications and variations of the methods and compositions
 described above will be obvious in view of the description of the invention.
 Such modifications are intended to be within the scope of the claims.

We claim:

1. A method for preparing cellulosic fibers with reduced flammability comprising:
 - a) preparing a composition comprising carboxylic acids but which does not include a phosphorous-based esterification catalyst or an alkoxide catalyst;
 - b) applying an effective, fire retarding amount of the composition to a substrate to be treated which comprises a cellulosic fiber or a blend of a cellulosic fiber with another fiber; and
 - 10 c) esterifying the carboxyl groups with a sufficient quantity of the hydroxy groups on the fiber to be treated such that the resulting treated fiber has an acceptable degree of fire resistance for the intended use.
2. The method of claim 1, wherein the carboxylic acid-containing composition comprises a C₂₋₂₀ straight chain, branched or cyclic alkane that
15 includes at least one carboxylic acid moiety, and which is optionally substituted with a functional group selected from the group consisting of carbon-carbon double bonds, halides, perfluorinated groups, amines, phosphorous esters, monosaccharides, polysaccharides, imides, and amides.
3. The method of claim 1, wherein the carboxylic acid-containing
20 composition includes an acid selected from the group consisting of maleic acid, malic acid, tartaric acid, succinic acid, citric acid, and maleic acid/acrylic acid co-polymers.
4. The method of claim 1, wherein the degree of substitution on the cellulosic substrate is between about 0.003 to 0.5.
- 25 5. The method of claim 1, wherein the degree of substitution on the cellulosic substrate is between about 0.005 to 0.025.
6. The method of claim 1 wherein the fiber is a cotton fiber.
7. The method of claim 6, wherein the cotton is in the form of a cotton carpet.
- 30 8. The method of claim 6, wherein the cotton is present in raised surface or lightweight apparel.

9. The method of claim 1, wherein the fiber is a blend of cotton and another fiber selected from the group consisting of polyesters, polyamides, polytrimethyl terephthalate (PTT), wool, acrylic, modacrylic, rayon, acetate, triacetate, polyolefins, Tencel®, and Lyocell.

5 10. The method of claim 1, wherein the composition further comprises a component selected from the group consisting of other fire retardants, dyes, wrinkle resist agents, de-foaming agents, buffers, pH stabilizers, fixing agents, stain repellents, stain blocking agents, soil repellents, wetting agents, softeners, water repellents, stain release agents,
10 optical brighteners, emulsifiers, and surfactants.

 11. The method of claim 1 wherein the fiber is selected from the group consisting of Lycell™, Tencel® and rayon.

 12. The method of claim 1 further comprising a dyeing step prior to or subsequent to the esterification step.

15 13. A carpet comprising cotton fiber in which a portion of the hydroxy groups on the cotton fiber have been esterified with a carboxylic acid-containing moiety.

 14. The carpet of claim 13, wherein the carboxylic acid-containing moiety is a C₂₋₂₀ straight chain, branched or cyclic alkane that includes at
20 least one carboxylic acid moiety, and which is optionally substituted with a functional group selected from the group consisting of carbon-carbon double bonds, halides, amines, phosphorous esters, monosaccharides, disaccharides, polysaccharides, amides and imides.

 15. The carpet of claim 14, wherein the carboxylic acid-containing
25 moiety is selected from the group consisting of maleic acid, malic acid, tartaric acid, succinic acid, citric acid, and maleic acid/acrylic acid co-polymers.

 16. The carpet of claim 14, wherein the degree of substitution on the cotton fiber is between about 0.003 to 0.5.

30 17. The carpet of claim 14, wherein the degree of substitution on the cotton fiber is between about 0.005 to 0.025.

18. The carpet of claim 14, wherein carpet further comprises a second fiber selected from the group consisting of polyesters, polyamides, polytrimethyl terephthalate (PTT), wool, acrylic, modacrylic, rayon, acetate, triacetate, polyolefins, Tencel®, and Lyocell.

5 19. The carpet of claim 14, wherein the carpet further comprises an additional fire retardant selected from the group consisting of metal oxides, metal carbonates, halocarbons, phosphorous esters, phosphorous amines, phosphorous salts, aluminum trihydrate, and nitrogen-containing compounds.

10 20. Raised surface or lightweight apparel comprising cotton fiber in which a portion of the hydroxy groups on the cotton fiber have been esterified with a carboxylic acid-containing moiety.

 21. A method for preparing cellulosic fibers with reduced flammability comprising:

- 15 a) preparing a composition comprising amino acids, proteins and/or peptides and a suitable crosslinking and/or coupling agent;
- b) applying an effective, fire retarding amount of the composition to a substrate to be treated which comprises a cellulosic fiber or a blend of a cellulosic fiber with another fiber; and
- 20 c) linking hydroxy, thiol, amine and/or carboxylic acid groups on the amino acid, protein and/or peptide with a sufficient quantity of the hydroxy groups on the fiber to be treated such that the resulting treated fiber has an acceptable degree of fire resistance for the intended use.

 22. The method of claim 21, wherein the amino acid, protein, peptide or crosslinking agent is substituted with one or more functional groups selected from the group consisting of carbon-carbon double bonds, halides, perfluorinated groups, amines, phosphorous esters, monosaccharides, polysaccharides, imides, and amides.

25 23. The method of claim 21, wherein the degree of substitution on the cellulosic substrate is between about 0.003 to 0.5.

30 24. The method of claim 21, wherein the degree of substitution on

the cellulosic substrate is between about 0.005 to 0.025.

25. The method of claim 21 wherein the fiber is a cotton fiber.

26. The method of claim 25, wherein the cotton is in the form of a cotton carpet.

5 27. The method of claim 25, wherein the cotton is present in raised surface or lightweight apparel.

28. The method of claim 21, wherein the fiber is a blend of cotton and another fiber selected from the group consisting of polyesters, polyamides, polytrimethyl terephthalate (PTT), wool, acrylic, modacrylic,
10 rayon, acetate, triacetate, polyolefins, Tencell™, and Lyocell.

29. The method of claim 21, wherein the fire-retardant composition further comprises an additional fire retardant selected from the group consisting of metal oxides, metal carbonates, halocarbons, phosphorous esters, phosphorous salts, phosphorous amines, aluminum trihydrate, and
15 nitrogen-containing compounds.

30. The method of claim 21, wherein the composition further comprises a component selected from the group consisting of other fire retardants, dyes, wrinkle resist agents, de-foaming agents, buffers, pH stabilizers, fixing agents, stain repellants, stain blocking agents, soil
20 repellants, wetting agents, softeners, water repellants, stain release agents, optical brighteners, emulsifiers, and surfactants.

31. The method of claim 21 wherein the fiber is selected from the group consisting of Lyocell™, Tencell™ and rayon.

32. A method for preparing cellulosic fibers with reduced
25 flammability comprising:

- a) selecting a suitable cellulosic substrate,
- b) pre-treating the substrate with a cationic pre-treatment,
- c) optionally removing excess pre-treatment,
- d) adding an effective, fire retarding amount of a composition
30 comprising amino acids, proteins and/or peptides and optionally including a suitable crosslinking agent and/or coupling agent to the pre-treated substrate,

and

- e) optionally linking hydroxy, thiol, amine and/or carboxylic acid groups on the amino acid, protein and/or peptide with a sufficient quantity of the hydroxy groups on the fiber to be treated such that the resulting treated fiber has an acceptable degree of fire resistance for the intended use, wherein the ratio by weight of the solution to the substrate is greater than 1:1.

33. The method of claim 32 further comprising a dyeing step in conjunction with or prior to the pre-treatment step.

34. A carpet comprising cotton fiber in which a portion of the hydroxy groups on the cotton fiber have been linked, directly or through a crosslinking agent, with an amino acid, protein and/or peptide.

35. The carpet of claim 34, wherein the protein is an enzyme.

36. The carpet of claim 34, wherein the degree of substitution on the cotton fiber is between about 0.003 to 0.5.

37. The carpet of claim 34, wherein the degree of substitution on the cotton fiber is between about 0.005 to 0.025.

38. The carpet of claim 34, wherein carpet further comprises a second fiber selected from the group consisting of polyesters, polyamides, polytrimethyl terephthalate (PTT), wool, acrylic, modacrylic, rayon, acetate, triacetate, polyolefins, Tencel™, and Lyocell.

39. The carpet of claim 34, wherein the carpet further comprises an additional fire retardant selected from the group consisting of metal oxides, metal carbonates, halocarbons, phosphorous esters, phosphorous amines, phosphorous salts, aluminum trihydrate, and nitrogen-containing compounds.

40. Raised surface or lightweight apparel comprising cotton fiber in which a portion of the hydroxy groups on the cotton fiber have been covalently linked, directly or via a crosslinking agent, with an amino acid, protein and/or peptide.

41. The apparel of claim 40 wherein the protein is an enzyme.

42. A composition comprising a cellulosic material in which between 5 and 100 percent of the hydroxy groups on the material are covalently linked with an amino acid, protein or peptide, directly or through the use of a crosslinking or coupling agent.

43. A method for preparing cellulosic substrates with reduced flammability comprising:

- a) preparing a composition comprising one or more crosslinking agents;
- 10 b) applying an effective, fire retarding amount of the composition to a substrate to be treated which comprises a cellulosic fiber or a blend of a cellulosic fiber with another fiber; and
- c) linking reactive groups on the crosslinking agent(s) with a sufficient quantity of the hydroxy groups on the fiber to be treated such that
15 the resulting treated fiber has an acceptable degree of fire resistance for the intended use.

44. The method of claim 43, wherein the crosslinking agent(s) is substituted with one or more functional groups selected from the group consisting of carbon-carbon double bonds, halides, perfluorinated groups, amines, phosphorus esters, monosaccharides, polysaccharides, imides, and amides.

45. The method of claim 43, wherein the degree of substitution on the cellulosic substrate is between about 0.003 to 0.5.

46. The method of claim 43, wherein the degree of substitution on the cellulosic substrate is between about 0.005 to 0.025.

47. The method of claim 43 wherein the fiber is a cotton fiber.

48. The method of claim 47, wherein the cotton is in the form of a cotton carpet.

49. The method of claim 47, wherein the cotton is present in raised surface or lightweight apparel.

50. The method of claim 43, wherein the fiber is a blend of cotton

and another fiber selected from the group consisting of polyesters, polyamides, polytrimethyl terephthalate (PTT), wool, acrylic, modacrylic, rayon, acetate, triacetate, polyolefins, Tencel®, and Lyocell.

51. The method of claim 43, wherein the fire-retardant composition
5 further comprises an additional fire retardant selected from the group consisting of metal oxides, metal carbonates, halocarbons, phosphorus esters, phosphorus salts, phosphorus amines, aluminum trihydrate, and nitrogen-containing compounds.

52. The method of claim 43, wherein the composition further
10 comprises a component selected from the group consisting of other fire retardants, dyes, wrinkle resist agents, de-foaming agents, buffers, pH stabilizers, fixing agents, stain repellants, stain blocking agents, soil repellants, wetting agents, softeners, water repellants, stain release agents, optical brighteners, emulsifiers, and surfactants.

15 53. The method of claim 43, wherein the fiber is selected from the group consisting of Lycell™, Tencel® and rayon.

54. The method of claim 43, wherein the fire-retardant composition further comprises a phosphorus-based compound.

55. The method of claim 54, wherein the phosphorus-based
20 compound is selected from the group consisting of vinyl phosphonate, bis(2-chloroethyl)vinyl phosphonate, tetrakis (2-chloroethyl)diphosphates, oligomeric phosphate-phosphonate, and bis(2-chloroethyl)2-chloroethylphosphonate.

56. A method for preparing cellulosic fibers with reduced
25 flammability comprising:

- a) selecting a suitable cellulosic substrate,
- b) pre-treating the substrate with a cationic pre-treatment,
- c) optionally removing excess pre-treatment,
- d) adding an effective, fire retarding amount of a composition
30 comprising one or more crosslinking agents to the pre-treated substrate, and
- e) optionally linking reactive groups on the crosslinking agent(s) with

a sufficient quantity of the hydroxy groups on the fiber to be treated such that the resulting treated fiber has an acceptable degree of fire resistance for the intended use,

wherein the ratio by weight of the solution to the substrate is greater
5 than 1:1.

57. The method of claim 56 further comprising a dyeing step in conjunction with or prior to the pre-treatment step.

58. The method of claim 56, wherein the composition further comprises a phosphorus-based compound.

10 59. A carpet comprising cotton fiber in which a portion of the hydroxy groups on the cotton fiber have been linked with a crosslinking agent.

60. The carpet of claim 59, wherein the crosslinking agent is a dimethyloldihydroxyethylene urea, imidazole, imidazolidinone, dialdehyde,
15 or a dichlorotriazine.

61. The carpet of claim 59, wherein the degree of substitution on the cotton fiber is between about 0.003 to 0.5.

62. The carpet of claim 59, wherein the degree of substitution on the cotton fiber is between about 0.005 to 0.025.

20 63. The carpet of claim 59, wherein carpet further comprises a second fiber selected from the group consisting of polyesters, polyamides, polytrimethyl terephthalate (PTT), wool, acrylic, modacrylic, rayon, acetate, triacetate, polyolefins, Tencel®, and Lyocell.

64. The carpet of claim 59, wherein the carpet further comprises an
25 additional fire retardant selected from the group consisting of metal oxides, metal carbonates, halocarbons, phosphorus esters, phosphorus amines, phosphorus salts, aluminum trihydrate, and nitrogen-containing compounds.

65. The carpet of claim 59, in which a portion of the hydroxy groups on the cotton fiber have been linked, directly or via a crosslinking agent, to a
30 phosphorus-based compound.

66. Raised surface or lightweight apparel comprising cotton fiber in

which a portion of the hydroxy groups on the cotton fiber have been covalently linked to a crosslinking agent.

67. The apparel of claim 66 wherein the agent is a dialdehyde or imidazolidone.

5 68. The apparel of claim 67 wherein a portion of the hydroxy groups on the cotton fiber have been linked, directly or via a crosslinking agent, to a phosphorus-based compound.

69. A composition comprising a cellulosic material in which between 5 and 100 percent of the hydroxy groups on the material are
10 covalently linked with a crosslinking agent.

70. An article of manufacture selected from the group consisting of protective clothing, children's sleepwear, upholstery, bedding, curtains, drapes and tents comprising cotton fiber wherein a portion of the hydroxy groups on the cotton fiber have been covalently linked to a crosslinking
15 agent and wherein a portion of the hydroxy groups on the cotton fiber have been linked, directly or via a crosslinking agent, to a phosphorus-based compound..

71. The article of manufacture of claim 70 wherein the crosslinking agent is a dialdehyde or imidazolidone.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/25997

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : DO6M 13/184, 13/207; DO5C 17/00

US CL : 8/120, 116.1, 115.7; 428/97

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 8/120, 116.1, 115.7; 428/97

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

USPAT, DERWENT, JPO, EPO

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US 5,733,750 A (LUND et al.) 31 March 1998, abstract; col. 1, lines 7-16; col. 2, lines 21-30 and lines 51-60; col. 2, line 67-col. 3, line 27; and col. 4, lines 32-35 and lines 58-60.	1-11, 13-20, 43-50, 52, 53, 59, 61-63, 66, and 69. -----12, 51, 54-58, and 64
X ----- Y	US 3,979,533 A (MOREAU et al.) 07 September 1976, abstract; col. 1, lines 13-55.	1, 2, 4-8, 43-49, 54, 69, 70 ----- 3, 9-12, 50-53, 55-58,



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	
A document defining the general state of the art which is not considered to be of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
B earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	*A* document member of the same patent family

Date of the actual completion of the international search

11 MARCH 2000

Date of mailing of the international search report

14 APR 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
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Authorized officer

CHERYL JUSKA

INTERNATIONAL SEARCH REPORT

 International application No.
 PCT/US99/25997

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X ----	JP 11-158774 A (MAE) 15 June 1999, abstract translation.	21-28, 40
P, Y		----- 29-39, 41, 42
Y	US 5,273,549 A (DIDIER et al.) 28 December 1993, abstract and col. 1, line 7-col. 3, line 34.	1, 2, 6-11, 43, 44, 47-54, 56-58, 69, 70.
A	US 5,696,528 A (YUN) 09 December 1997, abstract; col. 1, line 12-col. 3, line 62; col. 6, lines 39-55.	
A	US 4,095,945 A (UMETANI et al.) 20 June 1978, abstract; col. 1, lines 10-21 and lines 50-65; col. 5, line 63-col. 6, line 12.	
A	US 3,709,658 A (WALSH et al.) 09 January 1973, abstract and claims.	
A	US 4,600,606 A (MISCHUTIN) 15 July 1986, abstract.	
A	US 4,055,720 A (CHANCE et al.) 25 October 1977, abstract; col. 1, lines 6-18;	

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/25997

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☒ No protest accompanied the payment of additional search fees.

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-20, drawn to a carpet and raised surface apparel with reduced flammability, and to a method for preparing cellulosic fibers with reduced flammability, wherein said reduced flammability is a result of esterifying carboxyl groups with the cellulosic hydroxy groups.

Group II, claims 21-42, drawn to a carpet and raised surface apparel with reduced flammability, and to a method for preparing cellulosic fibers with reduced flammability, wherein said reduced flammability is a result of linking hydroxy, thiol, amine, and/or carboxylic acid groups of an amino acid, protein, and/or peptide with the cellulosic hydroxy groups.

Group III, claims 43-71, drawn to a carpet and raised surface apparel with reduced flammability, and to a method for preparing cellulosic fibers with reduced flammability, wherein said reduced flammability is a result of crosslinking reactive groups of a crosslinking agent to the cellulosic hydroxy groups.

The inventions listed as Groups I, II, and III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: each group produces reduced flammability in cellulosic fibers by a different chemical reaction.

